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(USSR) by A. N. Kharin

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IONIC EXCHANGE IN FRESH AND AGED HYDROSOLS
OF ARSENIC SULFIDE

By A. N. Kharin

As we know, ionic exchange plays an important part in the structural change of a binary electric layer of micelles and, in connection therewith, in the stability of colloid solutions. In the history of half a century of study of this problem it is possible to find very different viewpoints on rules governing ionic exchange in sols of arsenic sulfide. On many problems, especially that of the equivalence of ionic exchange, authors [1-18] often contradict each other. This impelled us to take up again the study of ionic exchange in the As_2S_3 sols, while taking into account all the material already collected on this subject. In spite of the opinion of various authors [20, 17 et al], we showed in our article [19] that arsenous acid discovered in As_2S_3 sols can never play the part of a strong acid. Solutions of As_2O_3 in water have a high pH value (of the order of 5-6). The total acid content in them cannot be determined neither by conductometric nor by potentiometric titration with alkali solutions and hence reference to the fact that acidification of aged sols (and the acidity of their ultrafiltrates) depends on arsenous acid, contradicts the data obtained by us on the properties of arsenous acid. Because of the insignificance of the acidic properties of As_2O_3 solutions, the processes for forming arsenite precipitates, for example by the equation: $2HAsO_2 + BaCl_2 \rightleftharpoons Ba(AsO_2)_2 + 2HCl$, seem rather improbable to us, since it would be difficult to admit that a very weak arsenous acid could, to an appreciable degree, and at the low value $pH \approx 3$, displace a strong hydrochloric acid.

Our experiment confirmed our opinion. After the addition of 5 cm³ of a 0.1 N solution of BaCl₂, CaCl₂ and MgCl₂ to 100 cm³ of a solution of chemically pure As₂O₃ (40 m-mol/l) not the slightest turbidity was discovered. Still less could arsenite precipitates be formed in acid intermicellar fluids of As₂S₃ sols. What strong acids appear in aging As₂S₃ sols? What complicates the ionic exchange in As₂O₃ sols? ^{what} And ^{is} the number of sorbed cations equivalent to the number of H⁺ ions forced out of the micells? These were the special questions for which we wished to find an answer in our work.

Method of Preparing and Studying As₂O₃ Sols

The As₂S₃ sols were prepared in the usual way: by passing H₂S through double distilled water [with a specific electric conductivity of (κ) 1-2·10⁻⁶ mho at 25°] while adding simultaneously an As₂O₃ solution saturated in boiling and cooled to various temperatures. The surplus H₂S was blown off by hydrogen passed through an alkalized solution of KMnO₄, through concentrated H₂SO₄ and through 2 Drexel flasks with distilled water. Hydrogen sulfide was obtained from ferrous sulfide by the action of sulfuric acid and washed through 3 flasks with doubly distilled water. An As₂O₃ solution was obtained from chemically pure As₂O₃ which did not leave a sediment after being heated on glass nor contain As₂O₅ [19]. Sol 8 was prepared with surplus As₂O₃; it did not have the odor of H₂S and was not blown off by hydrogen. Sols 9 and 11 (with some slight H₂S residues) are prepared in large quantities in 12 liter flasks of Pyrex glass (steamed after boiling water in them a long time). They were kept in these flasks, closed with corks, in contact with the air over them in the retorts. These sols were studied, both the fresh and the aged, under

various conditions (Table 2). The ionic exchange in them was studied at the same time.

Determination of the colloid As_2S_3 was carried out after coagulation of 100-200 ml of hydrochloric acid sol, as described in our article [19]. The article also described other methods used by us in studying sols: the determination of conductivity (at 25°), conductometric titration of sols and ultrafiltrates by alkali (at 25°), potentiometric determinations with glass electrodes, a method of preparing ultrafiltrates and obtaining ultrafiltrates (always reducing the volume of the sols two times) [22]. In addition, filtrates were studied after the coagulation of (20 ml) sols with hydrochloric acid (or NaCl); they were titrated by a 0.01 N solution of iodine to determine the substances which reduce iodine in an acid medium (H_2S , SO_2 and others).

To determine As_2O_3 , the acid filtrate was blown off with air (to eliminate H_2S , etc) and, after adding sodium bicarbonate, we titrated it with the same solution of iodine (sometimes we used the gravimetric method of control). Besides we tested the filtrates for their As_2O_5 content by boiling with HNO_3 and $(\text{NH}_4)_2\text{MoO}_4$ and other methods [22], and for their polythionic acid content (coagulation through the action of NaNO_3) through the action of AgNO_3 in the presence of HNO_3 when heated (after previously blowing off the H_2S , if any were discovered) [18]. Finally, after the coagulation of 100 ml of sol with hydrochloric acid, the SO_4^{--} in filtrates was determined by action of BaCl_2 solution.

Characteristics of Fresh and Aged Sols

Since we had already studied the first stage of changes in sols [19], the most interesting question now was what became of the sols in profound changes. It was especially interesting to ascertain what free strong acids were accumulated in sols in aging, together with weak arsenous acid, which appeared as a result of hydrolyzing As_2S_3 , thioarsenous and thioxyarsenous

acids, which stabilized the micelles and were unable to accumulate in a free state in acid solutions because of their instability [19].

The oxidation products of H_2S or As_2O_3 could be such free strong acids. Hence we directed our attention to the above-mentioned acids: $H_2S_xO_6$, H_2SO_4 , H_3AsO_4 and others (see method of study).

To speed up the aging process of As_2S_3 sols, we made use of the action of sunlight on the As_2S_3 sols in contact with the air [19]. Table 1 gives the results of the changes in sols A_1 and A_2 (sol A_2 was obtained from A_1 by adding to it a small quantity of As_2O_3 until an excess of the latter occurred). These changes took place for 110 days in retorts, closed with corks, with air in sunlight. During this time the sols disintegrated completely and over the precipitated sediment (As_2S_3 and sulfur) there was formed a completely colorless and transparent solution to which the data from the analysis of aged sols refer.

Table 1
Aging of As_2S_3 Sols in Contact with the Air in Sunlight

Sols	A_1	A_2	A_1	A_2
Age	1-2 days		110 days	
Storage Conditions	In the dark with air		In sunlight with air	
of sol $\times 10^5$ mhos	6.28	6.36	441	334
of ultrafiltrate $\times 10^5$ mhos	1.03	1.44		
Acidity of sol, m-equiv./l	0.54	0.52	22.75*	18.50*
Acidity of ultrafiltrate, m-equiv./l	0.04	0.04		
H_2S in filtrates, m-equiv./l	Traces	None	None	None
SO_4^{2-} " " "	None	none	22.8	18.56
As_2O_3 " " "	None	None	None	None
Polythionic acids, m-equiv./l	None	None	None	None

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As_2O_3 m-mol/l	None	1.05	19.0**	15.**
pH of sol	3.60	3.60	--	--
pH of ultrafiltrate	4.34	4.36	--	--
Colloidal As_2S_3 , gr/l	7.0	7.0	None	None

*Titration with a NaOH solution in the presence of methyl red gave 22.75 and 18.33 m-equiv./l.

**The gravimetric method gave 18.8 and 15.7 m-mol/l.

***As we found in a special experiment, when a pure As_2O_3 solution stands in sunlight in contact with the air, there is a slow accumulation of H_3AsO_4 . In the dark As_2O_3 does not acidify [22].

****By the gravimetric method 0.87 m-mol/l were obtained.

As may be seen from Table 1, the fresh A_1 (with excess H_2S) and A_2 sols (with excess As_2O_3) are almost identical and have very little ultrafiltrate acidity (and conductivity). After the disintegration of the sols the completely clarified fluids became very acid and their acidity coincided with the SO_4^{2-} content. Obviously, other strong acids were not formed under such conditions in As_2S_3 sols. Neither H_3AsO_4 *** nor polythionic acids appeared in them. Together with oxidation products $\text{H}_2\text{S}(\text{H}_2\text{SO}_4$ and S) in the sols there was an accumulation of arsenous acid, but it can ~~not~~ be titrated neither by conductometric nor by ordinary titration with alkali (with methyl red).

Table 2

Aging of As_2S_3 Sols in Contact with Air

No of Sol	8	9	9	11	11	11	11
Storage Conditions of sols and age	In dark, in contact with air						190 days in dark with air and 20 days in sunlight
	2 days	2 days	166 days	1 day	7 days	210 days	
of sols x 10^5 mhos	9.53	9.8	27.4	10.38	18.20	19.3	152.4
of ultrafiltrates x 10^5 mhos	7.15	4.67	15.82	3.22	5.22	6.15	121.0

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Acidity of sols, m-equiv/l	1.10	1.45	1.70	1.09	1.18	1.22	6.30
Acidity of ultrafiltrates m-equiv/l	Traces	0.06	0.50	0.07	0.13	0.27	5.31
H ₂ S in filtrates m-equiv/l	None	Traces	None	0.3	Traces	None	None
SO ₄ ⁼⁼ in filtrates, m-equiv/l	None	None	0.58	Traces	0.10	0.46	5.65
As ₂ O ₃ in filtrates, m-mol/l	20.0	None	0.84****	None	None	0.41	4.10
pH of sols	--	--	--	3.46	--	--	--
pH of ultrafiltrates	--	--	--	3.85	--	--	--
Colloid As ₂ S ₃ , gr/l	23.4	28.7	--	13.7	--	--	--

[For starred notes see previous page]

(*)In an article by Krestinokaya [20], there are indications that she also found H₂SO₄ in aged As₂S₃ sols.

Table 2 gives the characteristics of sols (both fresh and aged) with which experiments on ionic exchange were conducted: 8, 9, and 11. For example, Figure 1 shows the curves of conductometric titrations of sol and ultrafiltrate 9 with a solution of NaOH in the fresh and aged states at which their acidity was found to be that given in Table 2 and 3. The acidity of the other sols and ultrafiltrates was determined in the same manner.

It may be seen from Table 2 that sols 9 and 11, aged in the dark in contact with the air, were slightly acidified. The ultrafiltrates were noticeably acidified, and the accumulation of sulfuric acid in them was in close correspondence with this acidification. This was especially noticeable in the batch of sol 11, aged 210 days, 20 of these days being in the light. Everywhere, in accordance with the degree of "aging", arsenous acid accumulated, but nowhere arsenic, polythionic acids and acids which reduces iodine in acid medium were detected.

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Methods and Results of Investigation of Ionic Exchange

To clarify the problem of the process of ionic exchange in As_2S_3 sols and its complications, we determined the "acidification" which took place on adding $BaCl_2$ and $MgCl_2$ to the sols. For this purpose we determined the acidity of the filtrates obtained after the coagulation of 200 ml of sols with chlorides 20 to 24 hours after mixing. The determination was carried out by titrating 10-20 ml of the filtrate by a 0.01 N solution of NaOH from a microburette in the presence of methylred. The results of these titrations coincided with the results of potentiometric titrations with glass electrodes [22]. The conductometric method was not convenient in this instance because of the presence of salts in the filtrates. The results were recounted for a liter of sols.

From the acidity of the filtrates we subtracted the acidity of the ultrafiltrates obtained from separate parts of the sols by reducing the volume of sols two times. The ultrafiltrates were always prepared as described in previous articles [19, 21, 22]. The differences are shown in the last line of Table 3 under the heading "acidification".

From 100 ml of filtrates, after coagulation of the sols, we determined the residual concentration of Ba^{++} (by the weight of $BaSO_4$) and of Mg^{++} (by the weight of $Mg_2P_2O_7$). The number of absorbed cations was obtained from the difference between the original and final concentrations (calculated for a liter of sols).

In all these calculations the volume of the arsenic sulfide in the sols was not taken into consideration, as allowance for this volume changed the results only slightly (from 0.01 to 0.05 m-equiv./l), depending on the concentration of electrolytes and the arsenic sulfide. This lay within our limits of analytical errors (approximately ± 0.1 m-equiv./l).

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To allow for whatever number of cations were involved in the intermicellary fluid in the formation of insoluble salts, we took 100 ml of sols and added 10 ml of saturated solution of NaCl and filtered the coagulate. The same amount of BaCl_2 (MgCl_2) was added to 100 ml of the filtrate. After 24 hours, if a sediment formed, the sediment was filtered and the Ba^{++} (Mg^{++}) content in the filtrate was determined, and this content was recounted for 1 liter of sols allowing for all corrections for dilution by electrolytes. According to the difference in the amounts of Ba^{++} (Mg^{++}) introduced and final quantities, the quantity of combined in intermicellary fluid (in the filtrate) cation in m-equiv./l of sol was calculated.

Subtracting from the total amount of the absorbed cation in the sol the amount combined in the intermicellary fluid by chemical reactions, we obtained the quantity of cations sorbed in the micelles (Table 3).

To clarify the problem of the adsorption of the chlorine cations some experiments were conducted in which the concentrations of chlorine ions in the filtrates were determined after the coagulation of the sols with barium and sodium chlorides and hydrochloric acid. The results of these experiments are shown in Table 4. The concentration of Cl^- was determined after blowing off the filtrates with air (if H_2S) was present. Next we added to them HNO_3 and $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and a small surplus of a 0.1 N solution of AgNO_3 and proceeded to titrate the surplus of AgNO_3 with a 0.05 N solution of NH_2CNS from a microburette*.

*The sols contained nothing but H_2S in order to combine the Ag ion in the presence of HNO_3 of which we had been convinced by previous experiments; H_2S was completely eliminated by the blowing off.

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Table 3
Ion Exchange in As_2S_3 Sols During Aging

Added To 200 ml of Sols	Sol 8 age 2 days	Sol 9, age 2 days				Sol 9, age 166 days		Sol 11, age 7 days				Sol 11, age 310 days In the dark		Sol 11, age 310 days (20 of which were in the light)	
	10 ml 0.1N $BaCl_2$	10 ml 0.1N $BaCl_2$	10 ml 0.1N $HgCl_2$	10 ml 0.2N $BaCl_2$	30ml H_2O and 10ml 0.1N $BaCl_2$	30ml H_2O and 10ml 0.1N $HgCl_2$	1ml H_2O and 3ml 0.2N $BaCl_2$	1ml H_2O and 3ml 0.2N $HgCl_2$	9ml H_2O and 1ml 0.2N $BaCl_2$	9ml H_2O and 1ml 0.2N $HgCl_2$	40ml H_2O and 10ml 0.1N $BaCl_2$	40ml H_2O and 10ml 0.1N $HgCl_2$	40ml H_2O and 10ml 0.2N $BaCl_2$	40ml H_2O and 10ml 0.2N $HgCl_2$	
Original concentration of $Ba^{++}(Mg^{++})$ m-equiv/l of sol	5.0	5.0	5.0	10.0	5.0	5.0	3.0	3.0	1.0*	1.0*	5.0	5.0	10.0	10.0	
Weight of $BaSO_4$ ($Mg_2P_2O_7$) from 100 ml of the filtrate in grams**	0.0409	0.0409	0.0200	0.0898	0.0324	0.0180	0.0192	0.0094	0.0015	0.0013	0.0342	0.0190	0.0359	0.0416	
Equilibrium concen- tration of $Ba^{++}(Mg^{++})$ m-equiv/l of Sols	3.68	3.68	3.77	8.46	3.34	3.88	1.73	1.77	0.14	0.24	3.74	4.26	3.79	9.33	
Absorbed $Ba^{++}(Mg^{++})$ in Sols	1.32	1.31	1.23	1.54	1.66	1.12	1.27	1.23	0.86	0.76	1.26	0.74	6.21	0.67	
$Ba^{++}(Mg^{++})$ combined in intermicellar fluid of sols m-equiv/l of Sols...	0	0	0	0	0.67	0	0.04	0	0.04	0	0.46	0	5.51	0	
$Ba^{++}(Mg^{++})$ sorbed by micelles	1.32	1.32	1.23	1.54	0.99	1.12	1.23	1.23	0.82	0.76	0.80	0.74	0.70	0.67	
Acidity of Filtrates, m-equiv/l of Sols	1.16	1.43	1.39	1.49	1.63	1.63	1.32	1.28	0.84	0.86	1.13	1.13	6.04	6.04	
Acidity of Ultrafiltrates m-equiv/l of Sols	0	0.06	0.06	0.06	0.50	0.50	0.13	0.13	0.13	0.13	0.27	0.27	5.31	5.31	
"Acidification" of sols...	1.16	1.37	1.33	1.43	1.13	1.13	1.19	1.15	0.71	0.73	0.86	0.86	0.73	0.73	

* n^{++}/m^{++} was determined in ultra-

* During these concentrations the coagulation of the Sols was not complete; in these cases the $B^{++}(Mg^{++})$ was determined in ultrafiltrates.

** Control was exercised from 50 ml of the filtrate or, at times, by a second analysis of 100 ml of a filtrate from a new mixture.

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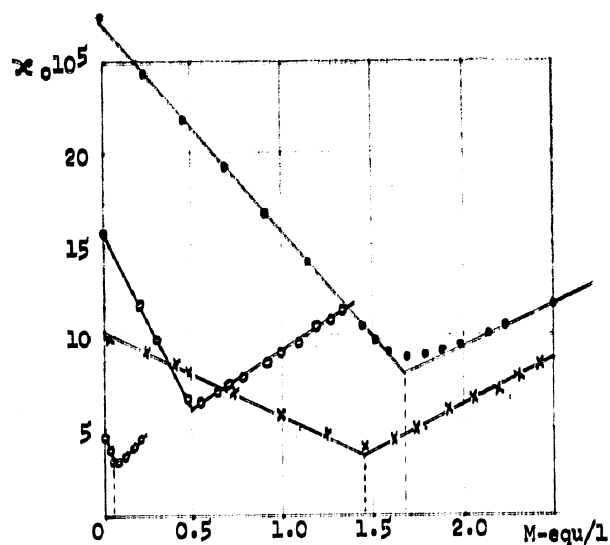


Figure 1. Conductometric titration curves of sol 9 with alkali;
 ---o---aged sol; ---o---aged ultrafiltrate; ---x--- fresh sol; ooo
 fresh ultrafiltrate

Table 4

Absorption of Chlorine Anions by As_2S_3 Sols

Added to 200 cm ³ of sols	Sol 11 (7 days)		
	7 cm ³ of H ₂ O and 3 cm ³ of 0.2 N Ba Cl ₂	20 cm ³ of HCl 0.1 N	20 cm ³ of NaCl 0.1 N
Original concentration of Cl ⁻ , m-equi/l	3.00	10.00	10.00
Equilibrium concentration of Cl ⁻	3.08	10.00	10.14
Absorbed Cl ⁻	+0.08	+0.10	+0.14
Original concentration of free acids in m-equi./l of sols	--	10.13	
Equilibrium acidity of sols	--	10.14	
Absorbed H ⁺ of ions		+0.01	

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Discussion of the Results

It is evident from all these data that, by introducing up to 10 m-equiv./l of barium or magnesium chlorides into fresh sols, the quantity of sorbed cations coincides within the range of accuracy of the determination (approximately ± 0.1 m-equiv./l) with the acidification of sols, one with the other, and, as the acidity of the ultrafiltrates from fresh sols is very slight, also with the acidity of the filtrates (and sols; see Table 2). This is identical with the observations of Rabinovich [4] and with the earlier observations of Whitney and Ober [2].

Obviously such a result is the consequence of: 1) the absence of the combining of cations in the intermicellary fluid of fresh sols and 2) the absence of "molecular" adsorption of chlorines on the sol micelles.

In these cases a clearly expressed ionic exchange takes place, uncomplicated by any other processes. With equal concentrations of salts exceeding the concentration of coagulation, a practically total displacement of the H^+ ions from the micelles is observed. If molecular adsorption of the chlorines takes place, an equivalent exchange is not observed; besides, adsorption of the Cl^- ions should be observed, which cannot be established by direct analyses of the filtrates. This coincides with the observations of Kargin [17], Whitney and Ober [2].

In aged sols the acidity of the ultrafiltrates is more marked than in fresh sols, and the acidification observed on adding barium and magnesium chlorides is less. The total quantity of absorbed Ba^{++} is close to the acidity of the filtrates (and sols), but the quantity of absorbed Mg^{++} is always less than the acidity of the filtrates (and sols) and less than the absorbed Ba^{++} .

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This difference in slightly aged sols (in the dark) is not very great (of the same order as in the experiment of Kargin [17]), but in the greatly aged 11 (in the light) this difference is very great. It is evident from Table 3 that Mg^{++} is never combined in the intermicellary fluid of aged sols, while Ba^{++} is always noticeably combined. If this quantity of combined Ba^{++} ions be taken into account and subtracted from the total quantity of ions absorbed by the sol, the difference in all cases will be in good agreement both with the "acidification" and with the quantity of sorbed magnesium ions. In our observations, carried out on old sols, the rules observed by Kargin [17] and partly also by Weiser [13] appeared very clear.

It is not difficult to understand that such results depend on the presence of H_2SO_4 in an intermicellary fluid of aged sols. The quantity of barium combined in the intermicellary fluid is in good agreement with the quantity of SO_4^{--} in sols. In sol 9, 0.67 m-equiv./l Ba^{++} is combined, and SO_4^{--} content in a sol is 0.58 m-equiv./l; in sol 11 (standing in the dark) 0.46 m-equiv./l of Ba^{++} combined and the SO_4^{--} content is the same; in greatly aged sol 11 Ba^{++} 5.51 m-equiv./l is combined, and the SO_4^{--} content in the sol is 5.65 m-equiv./l. These results mean that the Ba^{++} is combined in the intermicellary fluid only in the form $BaSO_4$. In the ultra-filtrates of aged sols 11 and 9, on adding $BaCl_2$, a sediment is formed which is not soluble in HCl , but on adding $MgCl_2$ a sediment is never formed. This agrees with our reason for the slowness of the probability of the formation of insoluble arsenites in acid solutions. Arsenites which are capable of being formed in small quantities, obviously, are also not absorbed completely on As_2S_3 particles.

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To sum up, it must be emphasized that, on adding BaCl_2 to aged sols, there takes place: first, an exchange of H^+ and Ba^{++} ions and, secondly, an interaction of BaCl_2 with H_2SO_4 in the intermicellary fluid.

Since the acidity of the sol is determined only by the sum of the micellary H^+ ions and by the free sulfuric acid (but not by arsenous acid), the quantity of combined barium always corresponds with the acidity of the sols and the filtrates from them (obtained after coagulation with barium chloride). Since Mg^{++} ions with SO_4^{--} ions yield a soluble salt and, also like Ba^{++} ions, do not form an arsenite precipitate, then on adding MgCl_2 to the sols a combination of Mg^{++} ions occurs only on account of the exchange of Mg^{++} with micellary H^+ ions. For this reason the amount of sorbed Mg^{++} in aged sols proves to be considerably less than the acidity of the sols and their filtrates and less than the quantity of absorbed Ba^{++} . But if the quantity of sorbed Mg^{++} be compared with the "acidification" and not with the acidity of the filtrates, as, in principle, many authors have wrongly done, the equivalence of the exchange of Mg^{++} ions with micellary H^+ ions will be discovered.

Our method of quantitative calculation of the combination of ions in the intermicellary fluid permits the deduction that Ba^{++} ions displace micellary H^+ ions equivalently both in aged and fresh sols*.

On adding to aged As_2S_3 sols Sr and Ca chlorides, such intermediate relations should be observed as those observed in adding, on the one hand, BaCl_2 and, on the other, MgCl_2 , in connection with the fact that the solubility of sulfates is increased in the series: BaSO_4 , SrSO_4 , CaSO_4 and MgSO_4 . These considerations, evidently, are in complete agreement with the results of the works done by various authors on aged sols.

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Conclusions

1. It has been demonstrated that in aging As_2S_3 sols in contact with the air sulfuric and arsenous acids are accumulated and that sulfuric acid conditions the acidification of the sols.

2. A simple method is offered for a quantitative calculation of the formation of insoluble salts on account of the reactions ~~which proceed~~ in the intermicellary fluid of the sols ^{which proceed} when electrolytes are added.

3. By using this method, it has been shown that the ionic exchange in aged As_2S_3 sols proceeds also equivalently in manner similar to that in fresh sols, although in aged sols it is complicated in some instances by intermicellary reactions.

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*A conclusion, like that reached by us in studying the ion exchange in sulfur sols [18].

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